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Development of Tough Alpha-SiAlON

I-Wei Chen
University of Pennsylvania, iweichen@seas.upenn.edu

Roman Shuba
University of Pennsylvania

Misha Y. Zenotchkine
University of Pennsylvania

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Keywords
SiAlON, fracture toughness, phase transformation, microstructure, nucleation

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I-Wei Chen, R. A. Shuba, and M. Y. Zenotchkine

Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, PA 19104-6272, USA

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Abstract

The development of tough α-SiAlON with elongated grains in the last five years is summarized. This progress has been guided by the improved understanding of phase relations and nucleation/growth kinetics in SiAlON ceramics. Although most α-SiAlON compositions can be processed to contain some elongated grains, their microstructure, fracture toughness and R-curve behavior vary greatly. Such variability is due to the different phase stability of α-SiAlONs and the varying physical chemistry of the competing phases, including the transient/residual liquid. For this reason, microstructure control of α-SiAlON must pay close attention to the composition, starting powder and heating schedule. Seeding with single crystals of an appropriate α-SiAlON composition provides an attractive alternative that simplifies the task of microstructure control, since such seeds are thermodynamically stable and they completely dominate the nucleation statistics. Tough and hard α-SiAlON ceramics containing Ca, Y, Nd, and Yb stabilizers have been obtained using this method, some with toughness exceeding 10 $MPam^{1/2}$. The ability of maintaining a uniform microstructure of highly elongated grains is the key to high toughness material.

Introduction

The practical interest in α-SiAlON primarily comes from the prospect of finding a harder ceramic than β-Si_3N_4 or β-SiAlON. The latter ceramics have excellent toughness, but their hardness, 14-16 GPa, is considerably lower than that of many other hard materials, including silicon carbide. Since many current applications of the silicon nitride ceramics are related to their high wear resistance, a harder material without compromising fracture toughness would clearly be attractive. High hardness of α-SiAlON (22 GPa) is an intrinsic material property, derived from the crystal structure of α-Si_3N_4, which has a longer stacking sequence (ABCD) than that (AB) of β-Si_3N_4. Such structure complexity increases the slip resistance of dislocations. Toughness, however, is not entirely an intrinsic property but is strongly correlated to the microstructure. Monolithic, non-transformable ceramics mainly derive their toughness from grain pullout near the crack tip. Therefore, a microstructure comprised of interlocking elongated grains is the most desirable for this purpose. The progressive development of such a microstructure coincides with the dramatic improvement in fracture toughness of β-Si_3N_4 over the last thirty years, as seen in Fig. 1.

Major milestones in this development are the innovations of Y-sintering aid [1], α-Si_3N_4-rich powders [2], gas pressure sintering [3], fiber-reinforcement concept [4] and controlled seeding [5]. Until rather recently, though, α-SiAlONs were known to have a microstructure of fine, equiaxed grains, hence low fracture toughness. Clearly, the path to tough α-SiAlON is through

the development of fiber-like microstructure with interlocking, elongated grains. This has been substantially achieved in the last five years. (See Fig. 1.)

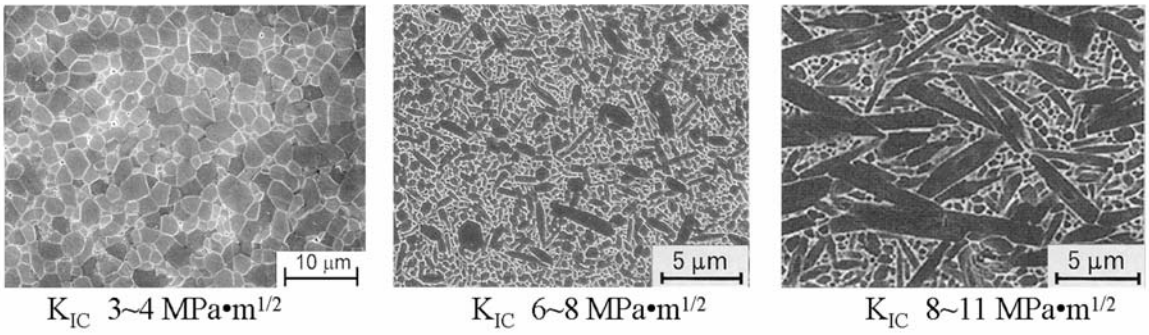

Figure 1: Progress in development of tough SiAlON materials.

Compared to β-Si_3N_4 and β-SiAlON, α-SiAlON is more complicated chemically. This is reflected in the wide range of phase stability of α-SiAlONs, and the large variety of physical chemical properties of the intervening phases that accompany the formation of α-SiAlON. Such complexity fundamentally influences the kinetics of microstructure evolution of α-SiAlON. The rapid development of tough α-SiAlON in recent years has been based upon a better understanding of chemical complexity of α-SiAlON systems. The present paper attempts to review our current understanding of the physical chemistry of α-SiAlON and its application to the development of tough ceramic.

Phase Stability of α-SiAlON

Alpha-SiAlON refers to the solid solution of α-Si_3N_4 with the general formula of $(M)_{m/z}Si_{12-(m+n)}Al_{(m+n)}O_nN_{(16-n)}$. Here, M is an interstitial cation of valence z. Like many other solid solutions in the (Si,Al)(O,N) family, there is the standard Al-O substitution of Si-N bond, hence the name SiAlON. In addition, there is Al substitution for Si, accompanied by interstitial (M) filling, in this structure. The phase relation of α-SiAlON may be examined using quaternary phase diagrams involving three cations (Si, Al, M) and two anions (O, N). To obtain a first understanding of the phase stability of α-SiAlON, however, it is easier to use simplified, though inadequate, phase representations. This is illustrated below with binary and ternary phase diagrams.

Figure 2 shows a schematic binary phase diagram between Si_3N_4 (m = 0, n = 0) and $M_{2/z}O$:3AlN (m = 8, n = 4), i.e., along the line of m = 2n. Here, α-SiAlON is shown as a eutectoid phase. Its lower solubility limit is nearly temperature independent, but its upper solubility limit expands with the temperature once above the eutectoid point. The range of the solubility tends to decrease with increasing the size of the interstitial cation, indicating a size effect on the stability of α-

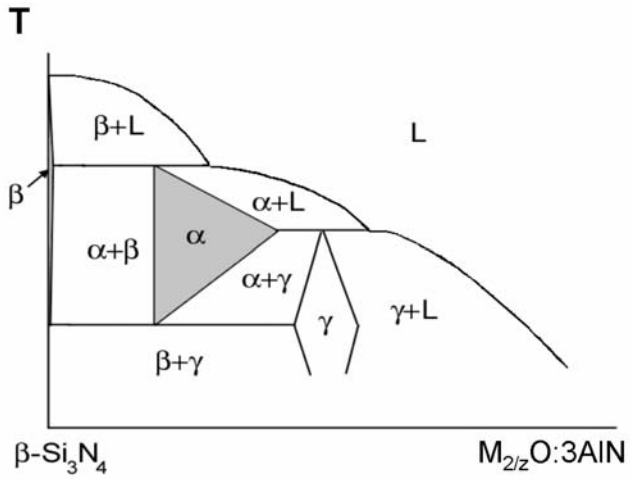

Figure 2: Pseudo-binary diagram indicating regions of stability of β-Si3N4 and α-SiAlON.

SiAlON. Without a solute, β-Si_3N_4 structure, shown as a line compound, is believed to be the stable phase at all temperatures of practical interest. This is consistent with the report by Mitomo and coworkers, who found α-Si_3N_4 to be metastable and transforming to β-Si_3N_4 at 2200 ^oC, once a liquid was introduced [6]. Below the eutectoid temperature, α-SiAlON decomposes to β-Si_3N_4 and some intermediate phase. In reality, the section along Si_3N_4 and $M_{2/z}O$:3AlN is not a pseudo-binary line. Therefore, the eutectoid temperature shown is not invariant because of the added (2) degrees of freedom, and altogether 5 phases (liquid, α-SiAlON, β-Si_3N_4 or β-SiAlON, and two another solids) can coexist at this temperature. Below the eutectoid temperature, the typical phases, coexisting with β-Si_3N_4 or β-SiAlON, are melilite ($M_2O_3Si_{3-x}Al_xO_xN_{4-x}$, which is also a SiAlON itself, here M is a rare earth cation) and AlN or one of its polytypoids (SiAlONs as well). The size effect also causes the eutectoid temperature to decrease with decreasing the size of interstitial cation. As a result, for α-SiAlONs with smaller interstitial cations, the eutectoid temperature is so low that the decomposition is not kinetically possible. In such case, single-phase α-SiAlON forms a stable ceramic suitable for practical applications.

The formula of α-SiAlON given above corresponds to a two-dimensional plane in the compositional space. This is commonly referred to as α'-plane. An isothermal section of a ternary phase diagram on Y-α'-plane is shown in Fig. 3 [7]. The vertices of the triangular plane are

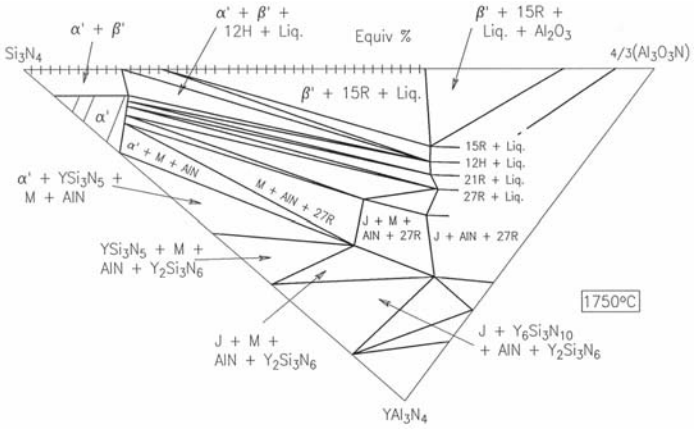

Figure 3: Isothermal section of a ternary phase diagram on Y-α'-plane.

Si_3N_4, Al_2O_3:AlN (m = 0, n = 12), and YN:3AlN (m = 12, n = 0). Without Y cation (m = 0), there is a solid solution of β-Si_3N_4 structure, namely β-SiAlON, that is formed by Al-O substitution of Si-N. It lies between Si_3N_4 and Al_2O_3:AlN. At the other limit (n = 0), there is oxygen-free α-Si_3N_4 solid solution, formed by $Si/M_{1/z}Al$ replacement. Such oxygen-free material is difficult to fabricate and will probably decompose upon oxidation. Single-phase α-SiAlON exists in an intermediate region between the above two limits. The α-SiAlON composition, that can be readily prepared using stable oxides and nitrides as starting powders, lies slightly above the line of m = 2n, between Si_3N_4 and $M_{2/z}O$:3AlN. As before, the α'-plane is not a pseudo-ternary section either. Therefore, additional phases, such as liquid, AlN polytypoids, and melilite, among others, that can not be represented by the formula $(M)_{m/z}Si_{12-(m+n)}Al_{(m+n)}O_nN_{(16-n)}$ and do not correspond to a single phase region on the α'-plane, can nevertheless coexist with the phases on the plane. This is evident by inspection of Fig. 3. Lastly, although Fig. 3 is an isothermal section, it is important to note, that single-phase region of α-SiAlON expands with increasing the temperature and with decreasing the size of the interstitial cation. In the case of Nd-SiAlON, for example, the α-SiAlON region shrinks with decreasing temperature and barely emerges above the m = 2n line at 1700 ^oC. Not surprisingly, Nd-α-SiAlON is unstable when held around 1400-1500 ^oC, as has been well reported. [8, 9]. For Mg-SiAlON, the α-SiAlON region is always below the m = 2n line for all practical temperatures. Therefore, it is not feasible to prepare single-phase Mg-α-SiAlON using common ceramic processing methods. In contrast, the single-phase region of α-SiAlON is large for Y-SiAlON and is especially large for Yb-SiAlON. These α-SiAlONs are entirely stable in the temperature range of practical interest.

Quaternary phase diagrams in the (M, Si, Al)(O, N) system are commonly represented as Janecke prisms. One of such diagrams [10] is shown in Fig. 4 (for M ≡ Y), in which α-SiAlON exists in a small area on the α'-plane near the Si_3N_4 corner. Once again, we emphasize that, unless the

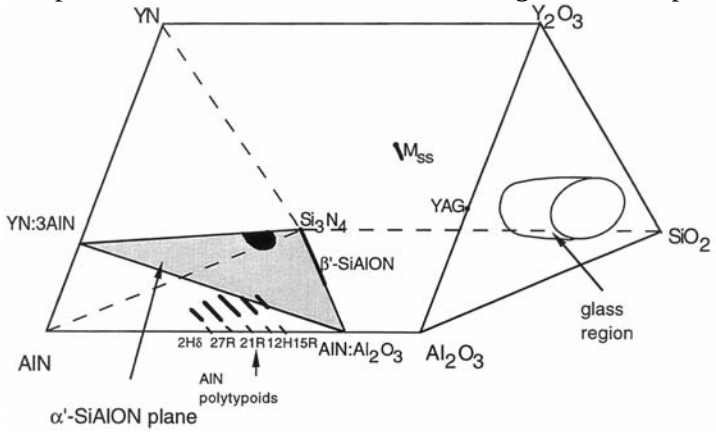

Figure 4: Janecke prism, showing the α'-plane and some of the phases known to coexist.

composition falls inside the single-phase α-SiAlON area, other phases, that are not on the α'-plane, will form in conjunction with α-SiAlON. This is shown, for example, in Fig. 5 for a composition that, while lying on the α'-plane, is also in the tetrahedron of α-SiAlON, β-SiAlON (both on the plane), 12H (below the plane) and liquid (above the plane) [11].

The observation that smaller interstitial cations impart greater phase stability to α-SiAlON may be related to vibrational entropy. Small cations of high field strength are known to strengthen oxide and oxynitride glasses. Such effect has been attributed to a strong bonding between

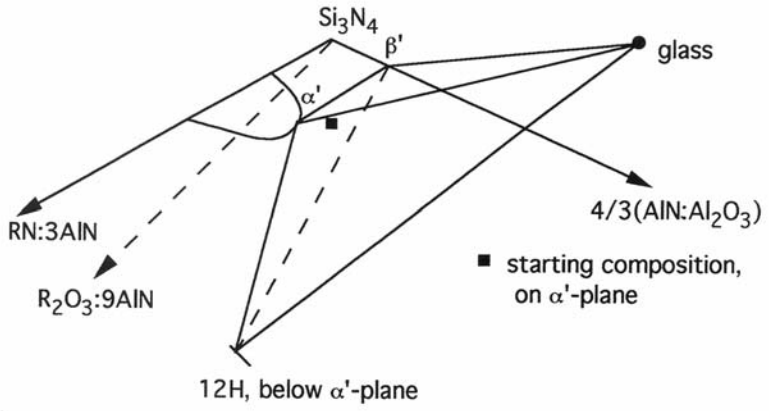

Figure 5: Schematic representation of a portion of the Janecke prism, showing that the intended α'-plane composition lies inside the α'-β'-AlN polytypoid (12H)-glass compatibility tetrahedron.

"interstitial" cations and the glass network. However, measurements of the lattice parameters of α-SiAlON did not show any size dependence within the experimental error, at least for rare earth interstitial cations. Therefore, the network structure of α-SiAlON is quite rigid, so that its enthalpic stabilization due to the interstitial-network bonding is relatively size independent. The fact that α-SiAlON is stable only at high temperature is also consistent with the notion of entropy stabilization. On the other hand, the free energies of α-Si_3N_4 and β-Si_3N_4 are very close to each other, the difference being within the experimental error of the current thermochemical experiments, as shown by Navrotsky and coworkers [12]. Also, like α-SiAlON, β-Si_3N_4 is stabilized by solid solution, forming β-SAlON. As a result, the single-phase region of α-SiAlON becomes considerably restricted by a competition with β-SiAlON.

Phase Transformation and Microstructure Development

Until quite recently, α-SiAlON ceramics were known for their ubiquitous microstructure of fine, equiaxed grains. Indeed, by taking advantage of this microstructure, Chen et al. developed the first superplastic SiAlON that could be biaxially stretched to 50% true strain at a strain rate of 10^{-4}/s [13]. These α-SiAlON ceramics were usually fabricated using powders that are rich in α-Si_3N_4 (above 90% of α-phase). The very high percentage of α-Si_3N_4 particles provided sites for heterogeneous nucleation of α-SiAlON, as clearly demonstrated by Hwang and Chen using TEM [14]. In this Symposium, Mitomo and coworkers reconfirmed the above TEM observation. They further showed that small β-Si_3N_4 particles tended to dissolve, while large β-Si_3N_4 particles tended to be trapped by growing α-SiAlON grains that had no epitaxial relation with the trapped β-Si_3N_4 particles. This is unlike the case of β-SiAlON nucleation, which can take place on α-Si_3N_4, β-Si_3N_4 and other transient β-SiAlON particles [15].

As a result of plentiful nucleation sites, α-SiAlON formation is easy and the final grain size after the phase transformation is small, usually comparable to that of the starting powder. Once formed, such a microstructure is relatively stable. This is because, after the phase transformation, the remaining driving force for microstructure evolution is interfacial energy, which leads to relatively slow Ostwald ripening. This case is similar to that of single-phase β-Si_3N_4 ceramics fabricated from β-Si_3N_4 powders. As shown by Mitomo and coworkers, such ceramics also have a stable microstructure of fine, equiaxed grains [16], and they are capable of superplastic

deformation. Mitomo and coworkers, however, showed that Ostwald ripening could still take place in these equiaxed β-Si_3N_4 ceramics when held at high temperatures, resulting in elongated grains. For α-SiAlON, such a process has only been observed in Ca-α-SiAlON [17]. This may be related to the higher viscosity in the most rare-earth-containing α-SiAlONs, which renders anisotropic grain growth difficult in dense ceramics. Other interface considerations could also be important as will become clear later.

The earliest published evidence of elongated α-SiAlON grains was that of (C.M.) Hwang and coworkers in α/β-SiAlONs using Sr and Y as additives [18]. Later, Huang and coworkers observed elongated grains in Li-Y/Ca-Y α-SiAlON compositions [19]. Shen, Nygren and coworkers conducted an extensive study to determine the relation between the composition and the microstructure [20]. They found some elongated α-SiAlON grains in high-(m,n) compositions, where the amount of (sometimes transient) liquid is large and the viscosity of the liquid is low. They also found that the tendency to form elongated α-SiAlON grains was enhanced when low Z rare-earth interstitial cations, such as Nd and Sm, were used [20, 21]. Lastly, Cheng and coworkers found elongated α-SiAlON grains in high-(m,n) compositions in Ca-SiAlON where, likewise, the amount of the liquid is high and the viscosity of the liquid is low [22]. These ceramics typically have lower hardness than what is commonly found in single-phase α-SiAlONs composed of fine, equiaxed grains.

The work of Chen and Rosenflanz using fine β-Si_3N_4 starting powders (0.5 μm) demonstrated, for the first time, that single-phase α-SiAlON with elongated grains can be obtained for all rare-earth-containing compositions (see Fig. 6) [23-26]. This is possible because of the lack of

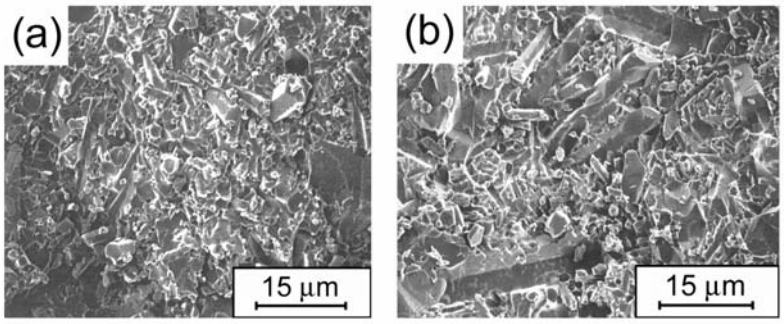

Figure 6: SEM micrographs of fracture surfaces, showing the material Nd-1209 prepared from (a) α-Si3N4 and (b) β-Si3N4 as starting powders.

nucleation sites in the powders. Without using high-(m,n) compositions and alkali/alkali-earth additions, the resultant ceramics are both hard and tough. They further found that the propensity for obtaining elongated grains increases with decreasing phase stability of α-SiAlON. Thus, Nd-α-SiAlON forms elongated grains most readily, while Yb-α-SiAlON does not form elongated grains under normal heating conditions. (See below.) This is also consistent with the observation that compositions near the α-SiAlON phase boundary form elongated grains more easily. The cause for the compositional effect lies in the nucleation kinetics: less stable α-SiAlON has a lower driving force for phase formation, hence a higher nucleation barrier and fewer viable nuclei. In the case of Yb-1212 (m=1.2, n=1.2), which has very high driving force, low nucleation rate can still be obtained by first holding at a low temperature (1550 ^{o}C) to reduce the kinetics,

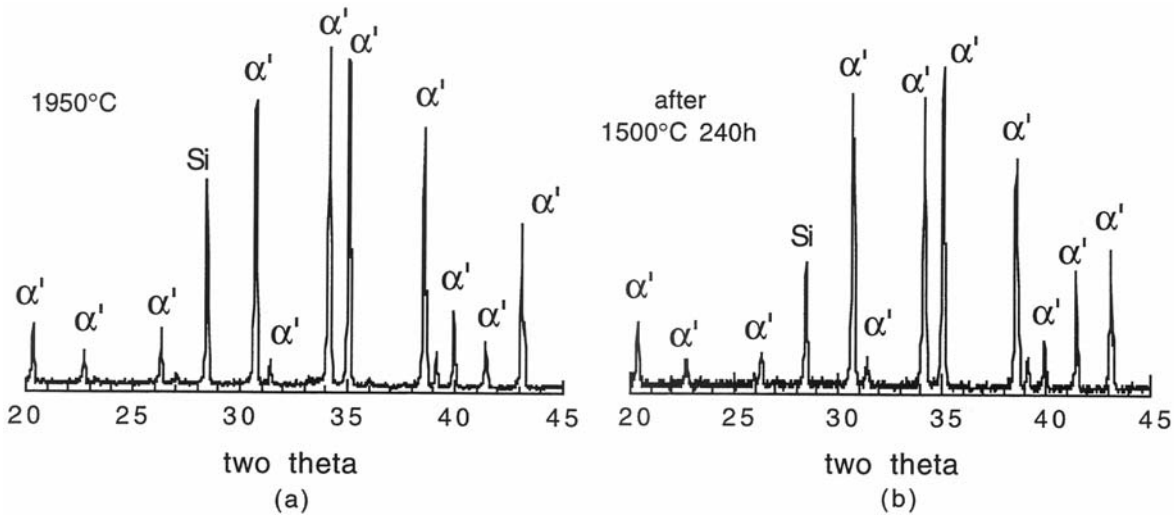

Figure 7: X-ray diffraction pattern for Yb-1212 composition, (a) equilibrated at 1950 °C and (b) annealed at 1500 °C for 10 days.

followed by holding at a high temperature (1950 ^{o}C) to grow elongated grains from the pre-formed nuclei. The stability of the resultant ceramic was finally verified by annealing at 1500 ^{o}C for 10 days showing no change in X-ray diffraction patterns. (Fig. 7) Seeding with α-SiAlON fragments to promote the growth of elongated grains was successfully performed as well. (See below.)

The concept of nucleation control was further extended to processing using α-Si_3N_4 powders [27]. Once again, α-SiAlON compositions, that are marginally stable, form elongated grains

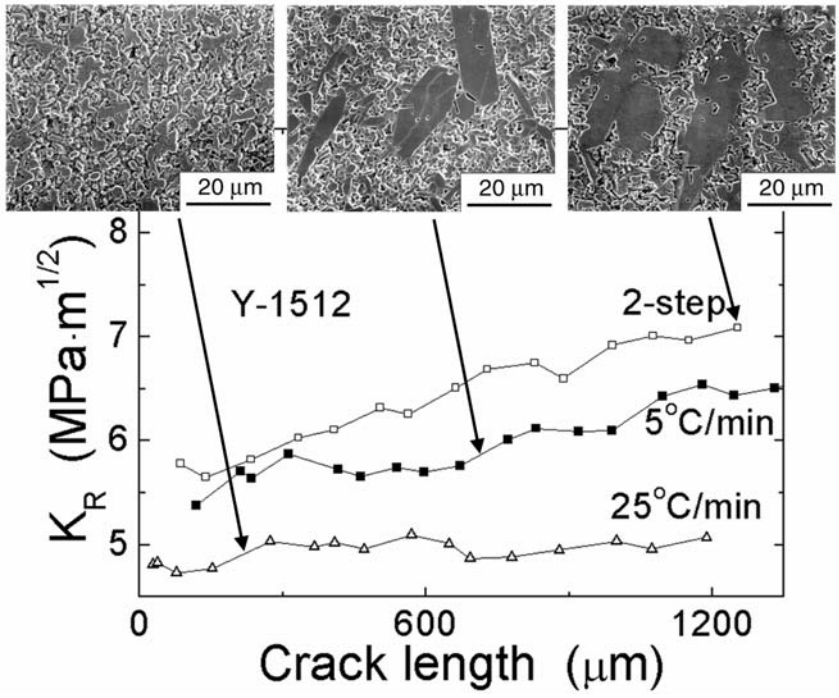

Figure 8: R-curves and SEM micrographs of unseeded Y-1512 following three heating schedules as shown.

more easily, while compositions that are more stable require the use of two-step firing, other variations of heating schedule, or α-SiAlON seeding to facilitate the formation of elongated grains. One example of the effect of heating rate and two-step firing on the microstructure and crack resistance curve (R-curve) of Y-SiAlON (m =1.5, n = 1.2) is shown in Fig. 8.

To summarize, the development of elongated grains in α-SiAlON is favored if (a) very few nuclei are available, and (b) the kinetics of crystal growth is fast. Of the above two conditions, nucleation control is critical for obtaining high toughness and hardness. It can be achieved by reducing the number of nucleation sites, lowering the driving force, or slowing the nucleation kinetics. The kinetics can be controlled by adjusting the amount of transient and/or residual liquid, its viscosity, and the particle type and size of the starting powder.

Seeding and Seeded Ceramics

The interplay of composition, temperature, and phase stability in α-SiAlON complicates the task of simultaneous control of nucleation and crystal growth. The task could be simplified if nucleation can be independently controlled, without regard to composition, temperature and, therefore, phase stability. For this purpose, Chen and coworkers have prepared α-SiAlON seed crystals, which were then added to the starting powders to form seeded ceramics [23-28]. Unlike most starting powders, such seeds are thermodynamically stable and do not dissolve. Therefore, they are highly effective in producing elongated grains. Direct evidence of elongated grains produced by seeding is readily visible in the sintered microstructure. One such example is shown in Fig. 9.

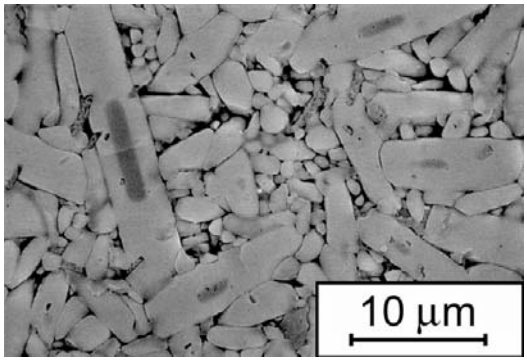

Figure 9: Backscattered SEM micrograph of Yb-1512 specimen seeded with 1 wt% of Y-1512.

Detailed investigation of seeding statistics in Y-α-SiAlON and Ca-α-SiAlON systems found that, when the concentration of seeds is small, there is very likely a one-to-one correspondence between the seed crystals and the elongated α-SiAlON grains observed. (See Fig. 10.) At higher concentrations of seed, elongated grains may impinge with each other and some seeds are rendered ineffective. Therefore, an optimal amount of seed needs to be determined to develop the most desirable microstructure (see below.) In all cases, however, it was confirmed, that the addition of α-SiAlON seed crystals almost completely removed the extraordinary sensitivity of the microstructure on composition and heating schedule, which is otherwise characteristic of all α-SiAlONs. For example, while different heating rates have produced in Y-1512 rather different microstructures and mechanical properties, as already shown in Fig. 8, very little difference is seen in Fig. 11 for the seeded ceramics fired at different heating rates.

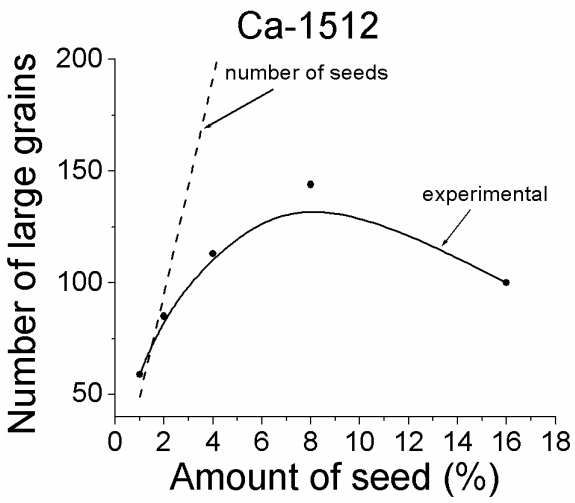

Figure 10: The measured number of large grains (experimental) and estimated number seeds revealed on a section.

The ability to exercise independent control of nucleation and crystal growth in the seeded ceramics makes it possible to investigate the effect of the SiAlON composition on the growth morphology. Shown in Fig. 12 are the microstructures of five α-SiAlON ceramics at 1% seeding. It can be seen that the grains in Ca- and Nd-SiAlONs are very thin and long, while those in Y- and Yb-SiAlONs are wider and less elongated. Furthermore, in Li-SiAlON only equiaxed grains are visible despite seeding. Of the above systems, Ca-, Yb-, and Li-SiAlONs are the most stable, while Nd-SiAlON is the least stable. So the stability does not necessarily correlate with the growth morphology. Similarly, Li- and Ca-SiAlON systems are likely to have the lowest liquid viscosity, whereas Yb-SiAlON system the highest viscosity. So the liquid viscosity does not directly correlate with the growth morphology either. As shown in Fig. 12, the only parameter that strongly correlates with the aspect ratio is the size of interstitial cation. This observation suggests that it is interface segregation that controls the growth morphology in seeded α-SiAlON.

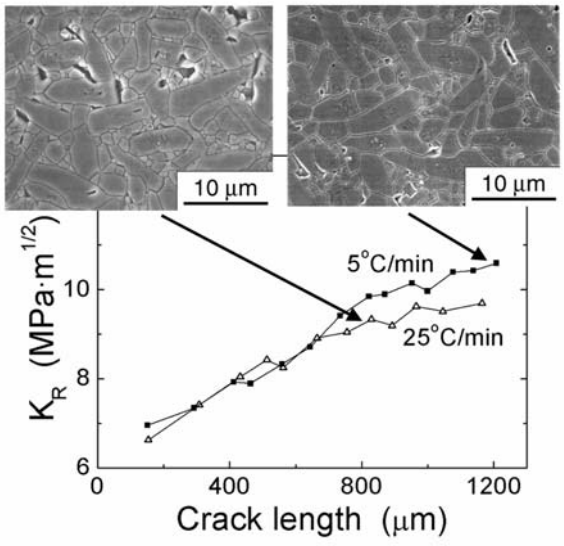

Figure 11: R-curves and SEM micrographs of seeded Y-1512 heated at two rates.

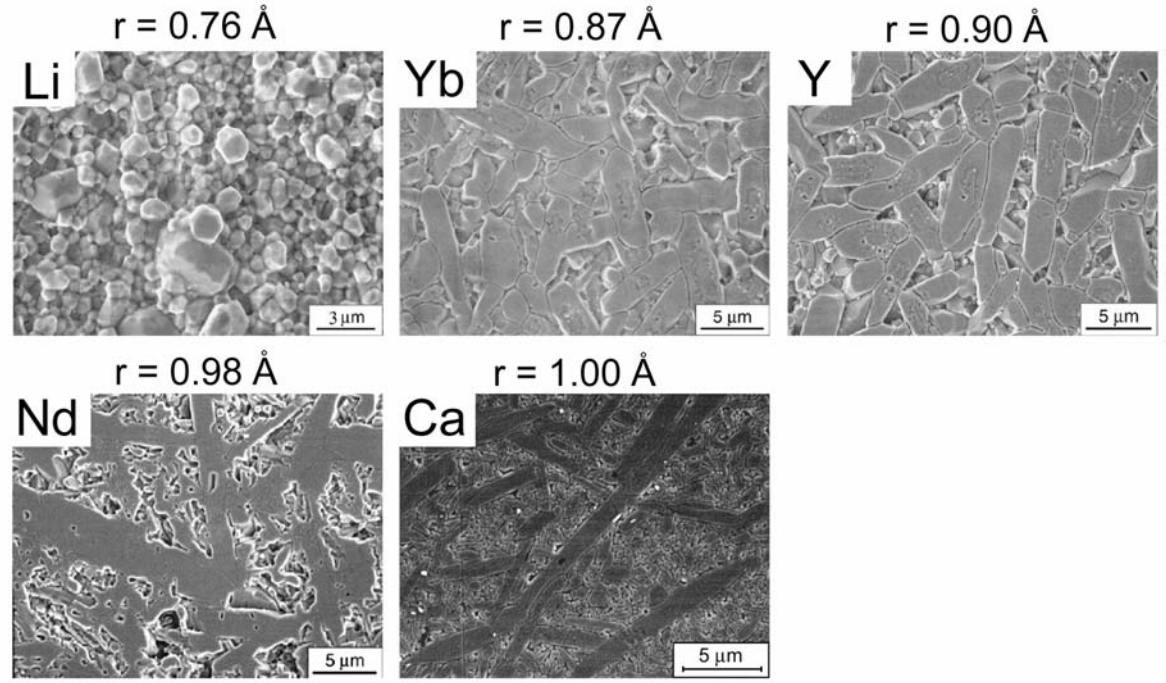

Figure 12: SEM micrographs of five α-SiAlONs (1512 composition) seeded with 1% of α-SiAlON of matching composition. The ionic radius of the interstitial cation is marked at the top of the micrograph.

A larger cation presumably segregates more strongly to the prismatic surfaces of the α-SiAlON grain, poisoning interface kinetics.

Optimization of Microstructure and Fracture Toughness

Like β-Si_3N_4, α-SiAlON derives its toughness primarily from grain pullout. Therefore, a coarser microstructure, including a larger grain width, should increase the fracture resistance regardless of aspect ratio. This is illustrated in Fig. 13, which shows that the progressive increase of the peak fracture toughness from the R-curve in Y-α-SiAlON and Ca-α-SiAlON (m =1.5, n=1.2 in both) is clearly correlated to the microstructure coarsening. (In particular, note the very fine acicular grains in Ca-SiAlON do not give rise to high toughness or rising R-curve.) On the other hand, it is also known that ceramics of coarse microstructures often have low fracture strengths. Therefore, microstructure optimization for mechanical applications should not be rested upon coarsening alone.

In seeded ceramics, the optimal microstructure judged by the optimal toughness is achieved at some optimal amount of seed. This amount is different in different systems as shown in Fig. 14. Out of the four compositions (all with m =1.5, n =1.2), the optimal amount of seed appears to fall into two ranges; 4-8% for Ca- and Nd-compositions and 1-2% for Y- and Yb-compositions. As shown in Fig. 15 for Ca-1512, the range of optimal seeding corresponds to the least statistical variation of the metrics of elongated grains. In other words, it is the most uniform microstructure that corresponds to the optimal toughness, rather than the microstructure that is the coarsest, or with the longest grains, or with the highest aspect ratio.

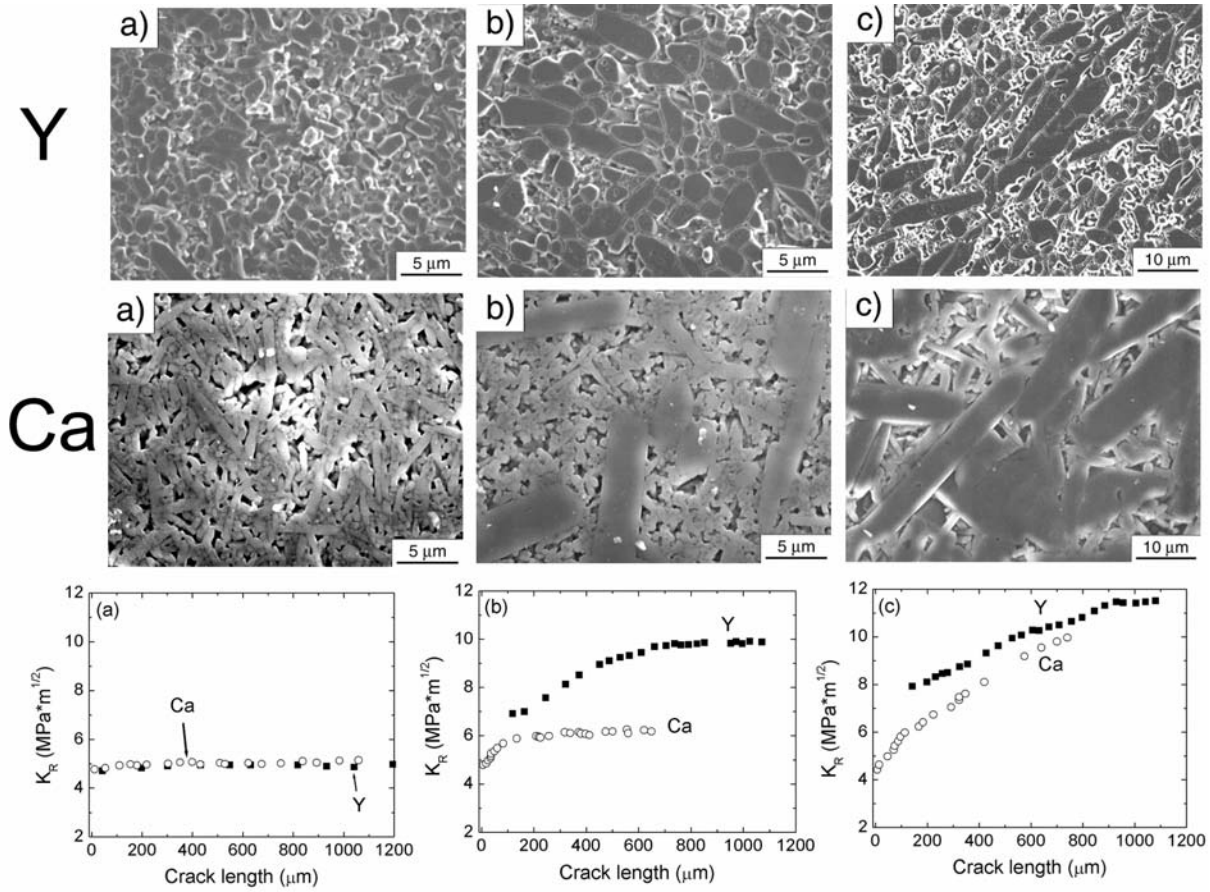

Figure 13: Correlation between coarsening microstructure (from left to right) and rising R-curve of Y-1512 and Ca-1512 α-SiAlONs.

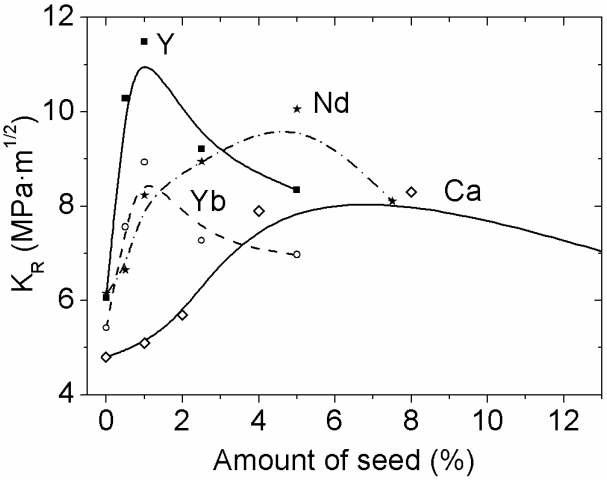

Figure 14: Peak fracture resistance on R-curve of four α-SiAlONs (1512 composition) seeded with various amounts of seed crystals, showing optimal microstructure and toughness is achieved at different amounts of seed for different SiAlON materials.

It was previously mentioned that Ca- and Nd-SiAlONs tend to have more slender grains than Y- and Yb-SiAlONs. This difference in grain morphology is related to the different amounts of seed,

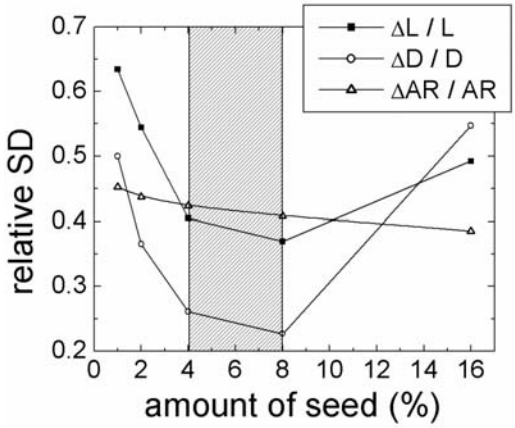

Figure 15: Relative standard deviation (SD), i.e., SD divided by mean of grain length (L), width (W) and aspect ratio (AR) as a function of seed amount.

required for optimal toughness in the two groups of ceramics. To appreciate the effect of grain morphology on the uniformity of microstructure, we illustrate in Fig. 16 two schematic microstructures, developed from the same concentration of seeds to the same area fraction of seed-produced α-SiAlON grains. Clearly, the microstructure with slender grains is less uniform.

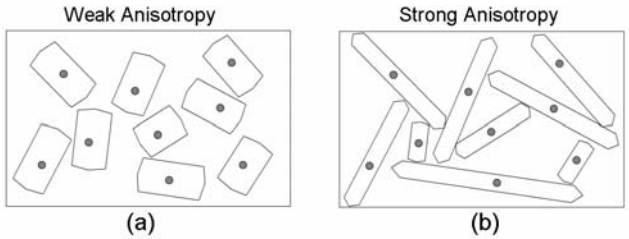

Figure 16: Two schematic microstructures with elongated grains growing in the same orientations from the same set of seeds. Grain width in (b) is half that of (a) but same area

Since a ceramic with non-uniform microstructure allows a crack to propagate in the regions of very few elongated grains, its fracture resistance is obviously not optimal. Optimization is to be achieved with highly interlocked, elongated grains, that fill the ceramic space tightly, which generally requires a higher concentration of grains when the aspect ratio is higher.

Summary

The rapid recent development of tough α-SiAlON has been guided by the appreciation and understanding of the phase relations and nucleation/growth kinetics of SiAlON ceramics. Due to the different phase stability of α-SiAlONs and the varying physical chemistry of the competing phases, microstructure control must be tailored for each α-SiAlON. Close attention to the composition, starting powder and heating schedule is thus needed. As an alternative, seeding, using single crystals of an appropriate α-SiAlON composition, provides an effective method that greatly simplifies the task of microstructure control. Alpha-SiAlON ceramics as tough as the best of β-Si_3N_4 ceramics, but much harder, have been developed using this method. The ability to maintain a uniform microstructure of highly elongated grains is the key to optimal toughness.

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References

[1] K. Komeya and H. Inoue, "Heat Resistant Strengthened Composite", Japanese Patent No. 703695 (1969).

[2] F. F. Lange, "Relations Between Strength, Fracture Energy, and Microstructure of Hot-Pressed Si_3N_4," J. Am. Ceram. Soc., Vol. 56, No. 10 (1973), p. 518-522.

[3] M. Mitomo, J. Mater. Sci., Vol. 11 (1976), p. 1103.

[4] E. Tani, S. Umebayashi, K. Kikobayashi and M. Nishijima, "Gas Pressure Sintering of Si_3N_4 with Concurrent Additives of Al_2O_3 and 5 wt% Rare Earth Oxides: High Fracture Toughness Si_3N_4 with Fiber-like Structure," Am. Ceram. Soc. Bull., Vol. 65, No. 9 (1986), p. 1311-1315.

[5] K. Hirao, T. Nagaokay, M. E. Brito, and S. Kanzaki, "Microstructure Control of Silicon Nitride by Seeding with Rod-like β-Silicon Nitride Particles," J. Am. Ceram. Soc., Vol. 77, No. 7 (1994), p. 1857-1862.

[6] H. Suematsu, M. Mitomo, T. E. Mitchell, J. J. Petrovic, O. Fukunaga, N. Ohashi, “The Alpha-beta Transformation in Silicon Nitride Single Crystals”, J. Am. Ceram. Soc., Vol. 80, No. 3 (1997), p. 615-620.

[7] Phase Diagram for Ceramists, Fig. 8774 (D), due to D. P. Thompson. American Ceramic Society (1994).

[8] Z. Shen, T. Ekstrom, and M. Nygren, "Homogeneity Region and Thermal Stability of Neodymium-Doped α-SiAlON Ceramics," J. Am. Ceram. Soc., Vol. 79, No. 3 (1996), p. 721-32.

[9] N. Camuscu, D. P. Thompson and H. Mandal, “Effect of Starting Composition, Type of Rare Earth Sintering Additive and Amount of Liquid Phase on $\alpha \leftrightarrow \beta$ Sialon Transformation”, J. Eur. Ceram. Soc., Vol. 17, No. 4 (1997), p. 599-613.

[10] Phase Diagram for Ceramists, Fig. 8773 (F), due to W.Y. Sun, T.Y. Tien and T.S. Yen. American Ceramic Society (1994).

[11] A. Rosenflanz and I-W. Chen, "Phase Relationships and Stability of α'-SiAlON," J. Am. Ceram. Soc., Vol. 82, No. 4 (1999), p. 1025-1036.

[12] J. J. Liang, A. Navrotsky, V. J. Leppert, M. J. Paskovitz, S. H. Risbud, T. Ludwig, H. J. Seifert, F. Aldinger, M. Mitomo, “Thermochemistry of Si(6-z)Al(z)O(z)N(8-z) (z=0 to 3.6) materials”, J. Mater. Res., Vol. 14, No. 12 (1999) 4630-4636.

[13] I-W. Chen and L. A. Xue, "Development of Superplastic Structural Cermaics," J. Am. Ceram. Soc, Vol. 73, No. 9 (1990), p. 2585-2609.

[14] S-L. Hwang and I-W. Chen, "Nucleation and Growth of α'-SiAlON on α-Si_3N_4," J. Am. Ceram. Soc., Vol. 77, No. 7 (1994), p. 1711-1718.

[15] S-L. Hwang and I-W. Chen, "Nucleation and Growth of β'-SiAlON, J. Am. Ceram. Soc., Vol. 77, No. 7 (1994), 1719-1728.

[16] Mitomo et al., "Fine Grained Silicon Nitride Ceramics Prepared from β-Powders," J. Am. Ceram. Soc., Vol. 78, No. 1 (1995), p. 211-214.

[17] C. A. Wood, H. Zhao, Y. B. Cheng, “Microstructural Development of Calcium Alpha-SiAlON Ceramics with Elongated Grains”, J. Am. Ceram. Soc., Vol. 82, No. 2 (1999), p. 421-428.

[18] C. J. Hwang, D. W. Susnitzky and D. R. Beaman, "Preparation of Multication α-SiAlON Containing Strontium," J. Am. Ceram. Soc., Vol. 78, No. 3 (1995), p. 588-592.
[19] Z. K. Huang, Y. Z. Jiang and T. Y. Tien, "Formation of α-SiAlON with Dual Modifying Cations (Li+Y and Ca+Y)," J. Mater. Sci. Lett., Vol. 16 (1997), p. 747-751.
[20] Z. J. Shen, L-O. Nordberg, M. Nygren and T. Ekstrom, "α-SiALON Grains with High Aspect Ratio – Utopia or Reality?", in Engineering Ceramics '96: High Reliability through Processing, ed. G.N. Babini, M. Haviar, and P. Sajgalik, p. 169-78 (Kluwer Academic Press, Netherland 1997).
[21] L-O. Nordberg, Z. Shen, M. Nygren and T. Ekstrom, "On the Extension of the α-SiAlON Solid Solution Range and Anisotropic Grain Growth in Sm-Doped α-SiAlON Ceramics," J. Eur. Ceram. Soc., Vol. 17 (1997), p. 575-580.
[22] H. Wang, Y-B. Cheng, B. C. Muddle, L. Gao and T.S. Yen, "Preferred Orientation in Hot-Pressed Ca α-SiAlON Ceramics," J. Mater. Sci. Lett., Vol. 15 (1996), p. 1447-1449.
[23] I-W. Chen and A. Rosenflanz, "A Tough SiAlON Ceramic Based on α-Si_3N_4 with a Whisker-like Microstructure," Nature, No. 389 (1997), p. 701-704.
[24] I-W. Chen and A. Rosenflanz, " *In-situ* Toughened Alpha Prime SiAlON-Based Ceramics," U.S. Patent No. 5,908,798 (1999).
[25] I-W. Chen and A. Rosenflanz, "Method of Making *In-situ* Toughened Alpha Prime SiAlON-Based Ceramics," U.S. Patent No. 6,139,791 (2000).
[26] A. Z. Rosenflanz, "α'-SiAlON: Phase Stability, Phase Transformations, and Microstructural Evolutions," PhD dissertation, University of Michigan (1997).
[27] J-S. Kim, A. Rosenflanz and I-W. Chen, "Microstructure Control of *In-Situ*-Toughened α-SiAlON Ceramics," J. Am. Ceram. Soc., Vol. 83, No. 7 (2000), p. 1819-1821.
[28] M. Zenotchkine, R. Shuba, J. S. Kim, I-W. Chen, “R-curve Behavior of *In-situ* Toughened Alpha-SiAlON Ceramics”, J. Am. Ceram. Soc., Vol. 84, No. 4, (2001), p. 884-886.